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ISOLATION OF BORON AND CARBON ATOMS IN CRYOGENIC SOLIDS

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ABSTRACT

Boron and carbon atoms, and their dimers and trimers were isolated in solid argon by co-condensation of their vapors onto a substrate maintained at 10 K. Growth and disappearance of various clusters with 3 to 12 atoms that occurred during annealing was studied by quantitative Fourier Transform Infrared Spectroscopy. The annealing experiments indicated that the initially formed solids contained about 80 % B and C atoms and BC molecules. At 5 mole percent atom concentration these High Energy Density Materials (HEDM) could be applied in propulsion where they are capable of producing about 25% higher specific impulse than the best rocket engines fueled by liquid hydrogen and liquid oxygen.

INTRODUCTION

Production of a cryogenic matrix with an atom density of $\sim 1 \times 10^{21}$ atoms cm^{-3} , which amounts to ~ 5 mole percent atoms in an inert solid, or an equivalent atom gas pressure of ~ 60 atm at 298 K, has been pursued under the auspices of the U. S. Air Force High Energy Density Matter (HEDM) Program [1]. Isolation of boron atoms in solid para hydrogen at ~ 4 K would produce a cryogenic solid propellant capable of providing around 25% larger specific impulse than that available from the best rocket engines fueled by liquid hydrogen and liquid oxygen. Thus, studies over the past decade have focused on production of matrices doped with lightweight atoms. To determine the fractional mass of dopant isolated as atoms, it is necessary to identify and measure the small clusters that inevitably must form upon warming of the matrix. Tam and Fajardo [2], using laser ablation of solid boron and uv/vis spectroscopy, isolated B atoms in rare gas and para-hydrogen solids at 4 K; they also identified B_2 in rare gas but not para hydrogen solids. *Ab-initio* calculations have shown [3] that B atoms have a 12 kcal/mol barrier for reaction with H_2 , but C atoms have no barrier [4] and could therefore never be isolated in solid hydrogen.

Currently, the Air Force Office of Scientific Research is supporting basic research on characterization of the states of aggregation of boron in cryogenic solids through the International Research Initiative administered by the European Office of Aerospace Research and Development, London. One product of this support, the first optical spectrum of the B_3 molecule, was recently reported and analyzed in detail [5]. This is an important contribution toward understanding boron HEDM because B_3 is a cyclic molecule so it probably resists attack by other atoms and radicals at low temperatures. B_3 is thought to be an “island of stability” beyond which further condensation could not occur in boron HEDM. Recent *ab-initio* studies and calculation of rate constants by RRKM theory [6,7] indicate that boron atoms, once isolated, would be stable in solid hydrogen.

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Key Word: High Energy Density Matter, HEDM, Boron Vapor, Boron Cluster, Matrix Isolation Spectroscopy

One of the greatest experimental difficulties with boron is caused by the extreme corrosiveness of liquid boron, which is a universal solvent. Under the auspices of the Small Business Innovative Research Program, the Air Force Research Laboratory recently developed a robust, high-flux boron vapor source for rapid preparation of ~ 100 mg samples of 5-mole percent B vapor in cryosolids in ~ 2 hours [8]. Here, a boron sphere inside a vacuum chamber is heated to melting by absorption of a beam of IR energy from an external cw CO₂ laser. A pool of liquid develops that is contained by solid. The vaporization process is self-regulated because the liquid surface reflects the laser energy, and vaporization occurs from the liquid at its melting point (2360 K) at a well-controlled flux. The cryosolid is produced in the usual way by co-condensation with rare gas or para hydrogen onto a substrate maintained at ~ 4 K.

BACKGROUND

The first experimental evidence of B_JC_{n-J} was reported 35-years ago by Verhaegen, Stafford, and Drowart [12]. They used mass spectrometry to study boron and boron carbide vaporization from graphite Knudsen cells that were heated by electron bombardment to temperatures up to 2500 K. The measured vapor pressure of boron at 2200 K was ~ 0.008 torr, 94% atoms, 5% BC₂, 1% B₂C, and 0.07% BC. At the same temperature, boron carbide had about one-half the vapor pressure with 96% atoms, 4% BC₂, 0.1% B₂C. Distributions of anions and cations of B_xC_y with up to 17-atoms have been measured in plumes of laser vaporized boron carbide targets by Becker and Dietze [13]. Their mass spectrometric analysis showed that B₂C⁻, B₂C⁺, BC₂⁻, and BC₂⁺ were major components of the plume. Matrix isolated BC₂ has been produced by oven and laser vaporization of carbon/boron mixtures and targets and measured by FTIR [9, 14] and ESR [15, 16] spectroscopy. More recently, Wyss, Grutter and Maier [17] isolated BC₂⁻ and BC⁻ in neon matrices by sputtering a boron carbide target with Cs⁺ and trapping the mass-selected anions in neon matrices. Neutrals were produced by electron photo-detachment with uv radiation. Electronic transitions of BC₂ and BC and their anions were studied. The FTIR spectrum of the previously identified [9] $\nu_2(a_1)$ fundamental of BC₂ was also observed. The infrared spectrum of BC has never been measured, but a CCSD(T)/cc-pVTZ calculation with quartic force field predicted [18] its vibrational fundamental at 1148 cm⁻¹ with intensity of 43 km mol⁻¹. Of the pure boron clusters, only B₃ has been experimentally observed. Li, Van Zee and Weltner [19] identified all four isotopomers of B₃ in argon matrices by FTIR spectroscopy and found that experimental frequencies matched *ab-initio* frequencies of its cyclic geometry. Although *ab-initio* studies of B_n, n > 4, have been carried out, only geometries and energies have been reported [20, 21]. Unlike C_n, B_n for n > 4 are predicted to have stable 3-dimensional geometries.

Carbon clusters were recently reviewed by Van Orden and Saykally [22]. Cyclic C₆ [23, 24], cyclic C₈ [25, 26], linear C₁₁ [27], have recently been identified by FTIR spectroscopy of clusters isolated in solid argon. Most recently, electronic spectra linear C₁₇, C₁₉, and C₂₁ [28] and cyclic C₁₀ and cyclic C₁₂ [29] isolated in neon matrices were reported, and Raman spectra of linear C₁₆, C₁₈, and C₂₀ were reported [30].

In this paper, qualitative and quantitative analysis of B_JC_{n-J} clusters in prototypical HEDM is presented up to clusters with J = 9. Previously, the first conclusive identifications of small boron clusters, BC₂, B₂C, BC₃, and B₂C₂, were reported [9-11] where observed FTIR fundamentals and isotope shifts were matched with predictions of *ab-initio* theory.

EXPERIMENTAL

Mixtures of boron and carbon powders were evaporated with a resistively heated oven to temperatures ~ 3000 K, and vapors were co-condensed with $\sim 1000:1$ excess argon at 10 K to form ~ 60 micrometers thick matrices in about one-hour. A precision matched pair of matrices was prepared as described in Ref. [9] with two different boron isotopic compositions and natural abundance carbon. Matrix (a) contained natural abundance boron, ¹¹B/¹⁰B = 4.0, and matrix (b) contained boron with an inverted isotope ratio, ¹¹B/¹⁰B = 0.37.

Each matrix had a [C/B] molar ratio of ~ 3.0 , a thickness of $\sim 60 \mu\text{m}$, and very similar absolute amounts of each element. Each matrix was annealed repeatedly to temperatures between 25 K and 40 K and spectra were recorded after each annealing as described in more detail below.

RESULTS AND DISCUSSION

Fig. 1 shows a Pascal's triangle representation of the boron/carbon cluster system. In the limit of statistical recombination of well mixed atoms, the relative yields of B_JC_{n-J} clusters of given n is given by

$$\rho(\text{B}_J\text{C}_{n-J}) / \rho(\text{C}_n) = n!/J!(n-J)![\text{B}/\text{C}]^J, \quad (1)$$

where $[\text{B}/\text{C}]$ is the molar ratio of boron to carbon, and $\rho(i)$ is the column density of species i .

Beer's Law enables quantitative analysis of the various species, $\rho_i = 2.303 A_i(\text{experiment})/I_i(\text{theory})$, where ρ_i is the average column density of species i , which is the average value of the product of the species density and matrix thickness. $A_i(\text{experiment})$ is the measured integrated intensity of the infrared absorbance of species i . $I_i(\text{theory})$ is the infrared absorption intensity of species i , which by necessity must be obtained by theoretical ab-initio calculation because experimental values are not available at this time. Fig. 1 indicates values of $I_i(\text{theory})$ for various clusters that were obtained by DFT/cc-pVDZ [31-34].

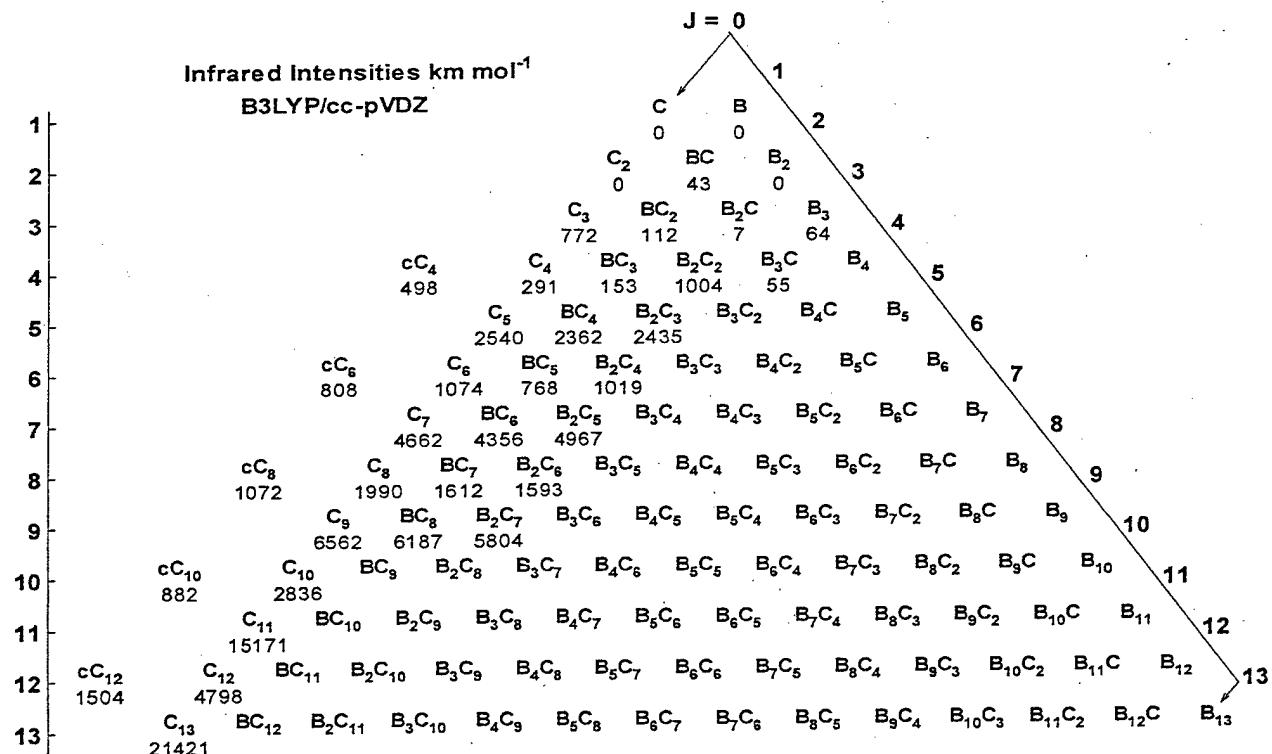


Figure 1. Representation of the B_JC_{n-J} ($n = 1 - 13$, $J = 0 - n$) system by Pascal's triangle. Numbers below molecular formulas denote the ab-initio intensities of the most intense infrared stretching fundamentals, Refs. [31] - [34]. Cyclic carbon clusters are removed from the triangle to the left.

Fig. 2 shows a survey spectrum of an annealed matrix with $\text{C}/\text{B} \sim 3$. Quasi-linear C_3 and cyclic BC_2 , B_2C , and B_3 , constituted about 80% of the total observable boron and carbon in the initially deposited matrix. Approximately statistical distributions [Eq. 1] among the $J = 0$, 1, and 2 clusters were measured in clusters with $n = 3$, 4, and 5 as discussed in greater detail below.

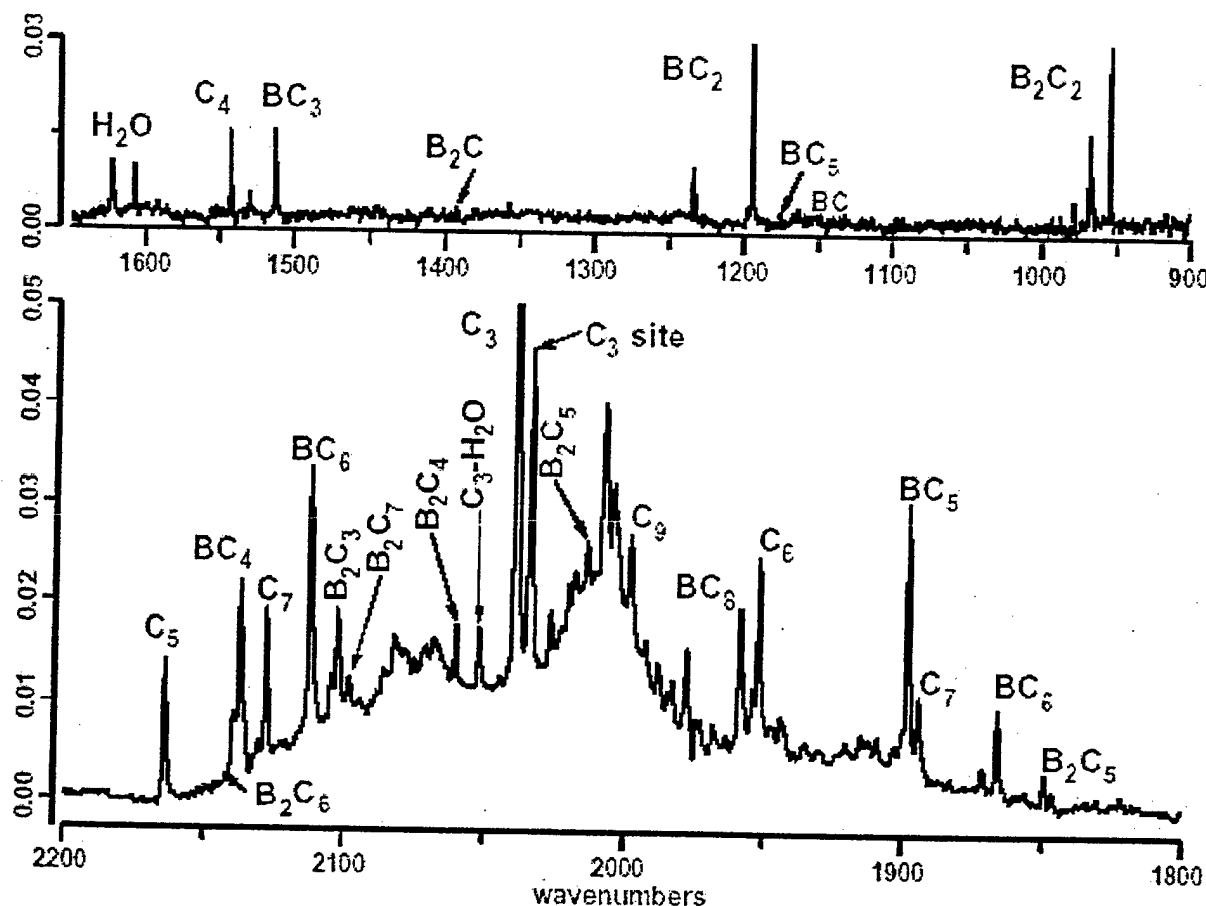


Figure 2. Survey spectrum of matrix containing carbon and boron clusters at natural isotopic abundance with $[B/C] \sim 1/3$ after three annealings. Fundamentals of BC_{n-1} for $n = 4, 5, 6, 7$, and 9 are similarly red-shifted from fundamentals of linear C_n , and their experimental absorbances are all slightly greater in this matrix. Two fundamentals of BC_6 are observed at 2112 and 1866 cm^{-1} , redshifted from the two fundamentals of linear C_7 .

Figure 3 shows the annealing behaviors of the FTIR bands belonging to BC_2 , BC_3 and B_2C_2 for each of the two precision matched matrices. BC_2 disappears entirely due to reaction at one of its carbon atoms with a radical species, which results in opening of the BC_2 ring. The dramatic appearance of B_2C_2 during the first annealing is consistent a mechanism involving recombination of BC , whose density lies below the limit of detection, or condensation of B atoms with BC_2 .

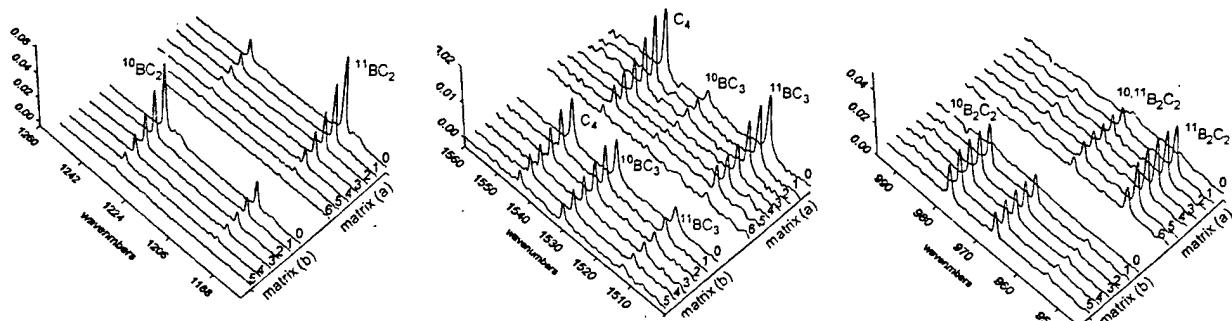


Figure 3. Absorbance spectra of matrix (a) and matrix (b) showing disappearance of BC_2 , BC_3 and C_4 , and appearance of B_2C_2 upon annealing. Spectra labeled "0" are spectra of originally deposited matrices. Annealing temperatures and times were (1) 27.5 K/150 s, (2) 30.0 K/75 s, (3) 32.5 K/45 s, (4) 35.0 K/30 s, (5) 37.5 K/20 s, (6) 40.0 K/20 s. The decrease in the peaks in the fifth and sixth annealing is due to matrix sublimation. The red-shift of the BC_3 absorption from the C_4 absorption is indicative of red shifts observed for all the other BC_{n-1} clusters when a boron atom is substituted for a carbon atom in a C_n cluster.

Fig. 4 shows the annealing behaviors of the $^{11}\text{B}_J^{12}\text{C}_{n-1}$ clusters, $n = 3$ to 9 and $J = 0, 1, 2$ that were measured in matrix (a). Loss of clusters during the sixth annealing by matrix sublimation is generally greatest for C_n

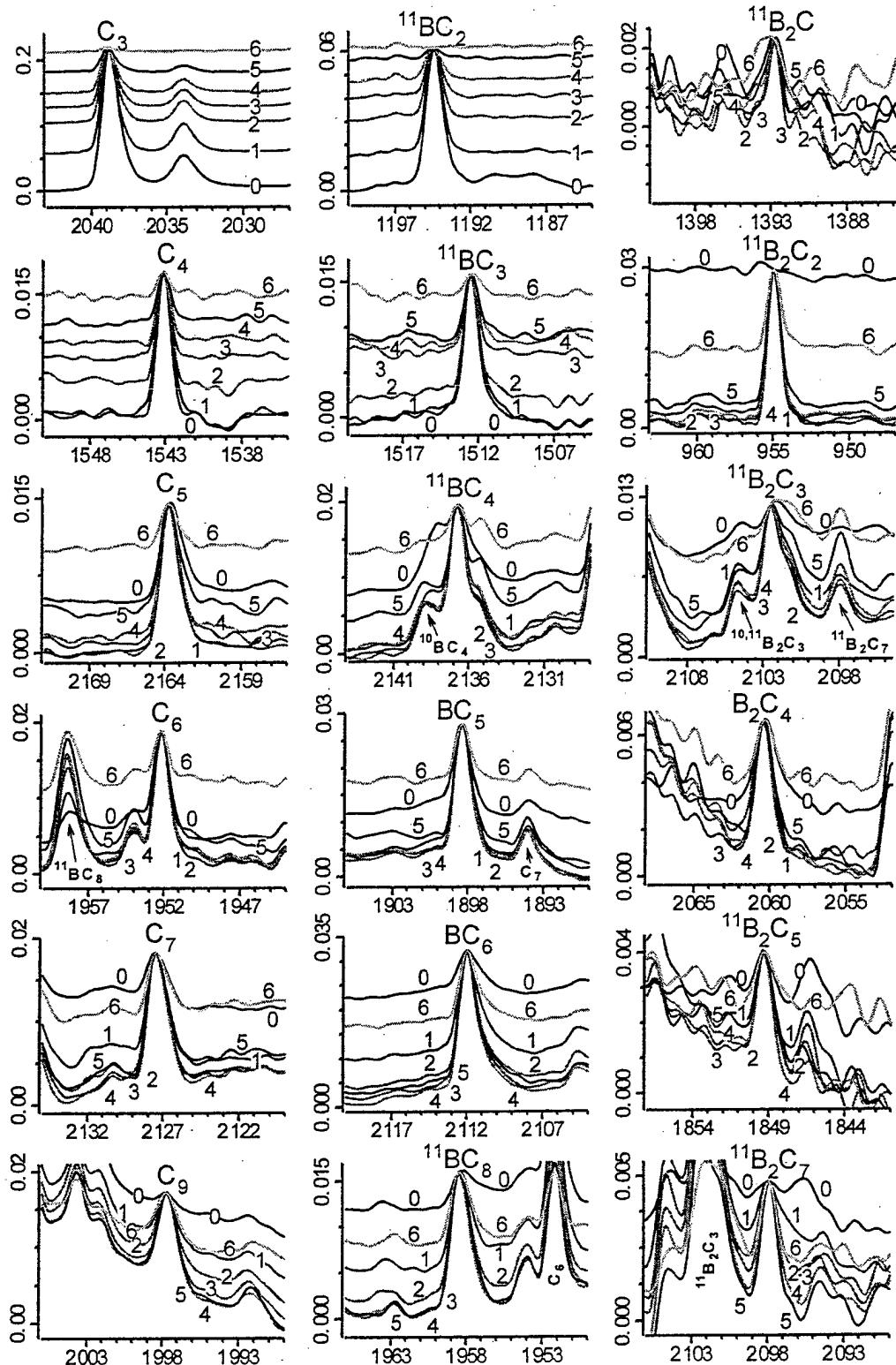


Figure 4. Annealing behaviors of B_JC_{n-J} species in matrix (a). Spectra labeled '0' were obtained from the originally deposited matrix, and spectra labeled '1' to '6' were obtained after successive annealings as detailed in the Fig. 3 caption. Absolute absorbance scales, $A_{\text{exp}}(i) = -\log_{10}(\text{transmittance})$, are offset to force coincidence at the peak maxima. Boron isotopomers of BC_5 , BC_6 and B_2C_4 are unresolved. The weaker of two bands of B_2C_5 ($I_{\text{theory}} = 1034 \text{ km mol}^{-1}$, at 1850 cm^{-1}) is shown here. Spectral resolution is limited to $\sim 1 \text{ cm}^{-1}$ by matrix broadening. The lower detection limit is $A_{\text{exp}}(i) \sim 0.001 \text{ cm}^{-1}$.

and smallest for B_2C_{n-2} , which is consistent with a stratified matrix with a higher [C/B] ratio near the subliming surface. Apparently, boron evaporates more rapidly than carbon during the early stage of evaporation, resulting in boron-rich layers near the substrate.

The distribution of the $n = 3$ clusters showed that their column densities are in the ratio $\rho(C_3): \rho(BC_2): \rho(B_2C): \rho(B_3) = 1.0:1.5:0.5:< 0.05$, where only the upper limit for $\rho(B_3)$ may be determined because it was not observed. This is consistent with statistical formation of the trimers by condensation from well-mixed atoms in a matrix with $[B/C] \sim 1/3$, which would produce a $1.0:1.0:0.33:0.05$ distribution, Eq. 1. Agreement between distributions implies trimers form by random condensation of well-mixed atoms, uninfluenced by the relative energies of the trimers, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics. Linear C_3 and cyclic BC_2 , disappeared entirely when the matrices were repeatedly annealed to temperatures between 25 K and 35 K, but cyclic B_2C was inert. Linear C_4 and BC_3 (BCCC) disappeared more slowly, and linear B_2C_2 (BCCB) grew to $\sim 95\%$ of its final value during the first annealing. Once formed, B_2C_2 , like B_2C , was also inert to further reaction.

Figure 5 shows the absolute column densities of the analyzed clusters that were obtained by transformation of the Fig. 4 data with Beer's law and theoretical intensities shown in Fig. 1. The BC molecule was not observed, but its upper limit column density was established to be about equal to that of the B_2C_2 . Thus, recombination of BC cannot be ruled out as the source of B_2C_2 .

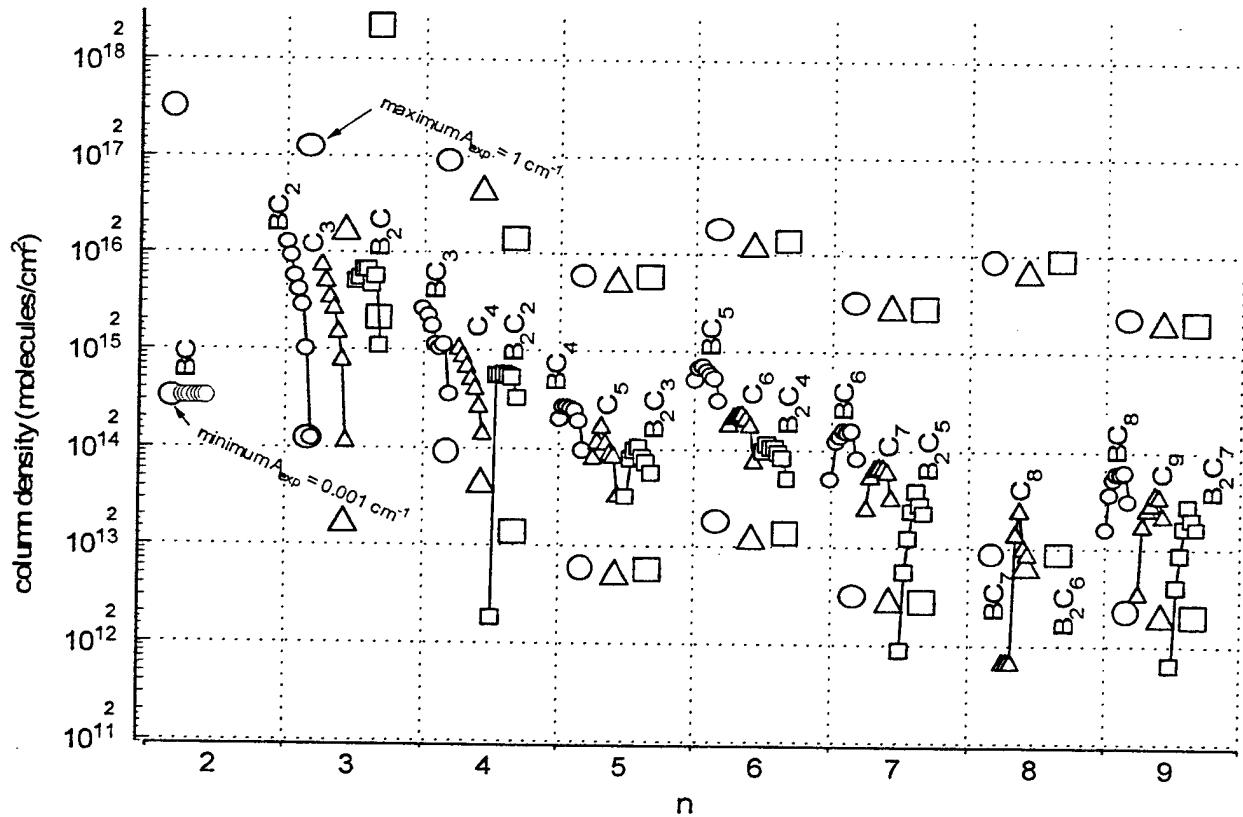


Figure 5. Distributions of B_JC_{n-J} clusters, $J = 0, 1, 2$; $n = 3 - 9$. Circles, triangles and squares represent BC_{n-1} , C_n , and BC_{n-2} clusters, respectively. Large symbols denote upper and lower limits of measurement, based on a nominal minimum measurable absorbance of 0.0023 cm^{-1} , and a maximum absorbance for linearity of Beer's law of 2.3 cm^{-1} (1% transmittance). Small symbols denote measured quantities in the initial matrix, and in six annealed matrices. Some of the larger clusters ($n = 8, 10, 11$) have not been identified, BC_7 , B_2C_6 , BC_9 , B_2C_8 , BC_{10} , B_2C_9 .

In previous work [23, 25] on carbon matrices, annealing led to disappearance of atoms, dimers and trimers from the initial deposits. The identified products of recombination included cyclic C_6 and cyclic C_8 , and linear C_n molecules, $4 < n < 13$. After annealing to constant composition, the total measurable carbon was

found to be as much as twice the initial measurable carbon, indicating that about 50 % of the initially deposited carbon was isolated as atoms and dimers. The cyclic molecules, the dominant condensation products, amounted to as much as ~ 60% of total carbon in the fully annealed matrix.

In matrices containing boron, linear C_3 , cyclic BC_2 , B_2C , and B_3 , constituted about 80% of the total observable boron and carbon in the initially deposited matrix. Observation of approximately statistical distributions [Eq. 1] in clusters with $n = 3, 4$, and 5 in the initially deposited matrices implies that these smaller clusters form by random condensation of well-mixed atoms. C_3 and BC_2 disappeared entirely when the matrices were repeatedly annealed to temperatures between 25 K and 35 K, but cyclic B_2C was inert. Linear C_4 and BC_3 (BCCC) disappeared more slowly, and linear B_2C_2 (BCCB) grew to ~ 95% of its final value during the first annealing. Once formed, B_2C_2 , like B_2C , was inert to further reaction.

The sources of B_2C_2 are from condensation of atom plus trimer ($B + BC_2$ but not $C + B_2C$) or dimer + dimer ($BC + BC$ but not $B_2 + C_2$). Although BC was not observed, the upper limit of $\rho(BC)$ is larger than $\rho(B_2C_2)$ so that BC cannot be ruled out as a source of B_2C_2 . The growth of B_2C_2 is conclusive evidence of the presence of BC and/or B in the originally deposited matrix in an amount at least as great as the growth of B_2C_2 .

Linear C_5 , BC_4 (BCCCC) and B_2C_3 (BCCCB) and larger linear clusters (B_3C_{n-J} , $5 < n < 11$, $J = 0, 1, 2$), all grew upon annealing. The sources of B_2C_3 are dimer + trimer ($BC + BC_2$ but not $B_2 + C_3$) and atom + tetramer ($B + BC_3$ but not $C + B_2C_2$). Since $\rho(BC_2) \sim 5\rho(BC_3)$ in the initially deposited matrix, the $BC + BC_2$ source is dominant. Growth of B_2C_3 conclusively establishes the presence of BC in the matrix in an amount at least as great as the amount by which B_2C_3 grows.

Growth of BC_4 occurs primarily by $BC + C_3$ rather than $B + C_4$ or $C + BC_3$ because $\rho(C_3) \sim 10\rho(C_4)$ and $\rho(C_3) \sim 2\rho(BC_3)$. Growth of C_5 occurs by $C + C_4$ and $C_2 + C_3$, which establishes the presence of C and/or C_2 in the original matrix in an amount at least as great as C_5 growth.

CONCLUSIONS

Disappearance of triangular BC_2 requires breaking of one of its B-C bonds when one of its carbon atoms is attacked. The major reorganization of electronic energy involved in opening the ring appears to occur with little ($< \sim 3$ kcal mol $^{-1}$) or no energy barrier, which makes this small molecule a candidate for an interesting *ab-initio* study of unusual reactivity at low temperature. Annealing kinetics of disappearance of C_3 and BC_2 , and of appearance of B_2C , C_4 , BC_3 , B_2C_2 , C_5 , BC_4 , and B_2C_3 unequivocally establishes the presence of atoms and dimers in the originally deposited matrix. About 80% or more of the initially deposited HEDM existed as atoms, dimers and trimers. Molecules with two boron atoms are immune from radical attack and condensation during annealing.

B_2C_{n-2} clusters, once formed, were inert to further condensation upon annealing. Thus, energy loss by recombination during preparation of high energy density matrices (HEDM) is minimized in matrices with large B/C ratios. For example, when B/C ~ 2, any recombination that does occur during co-deposition would tend to produce B_2C , which is an inert molecule. In pure boron HEDM, the cyclic B_3 molecule may be similarly inert, which would suggest that energy loss by recombination will also stop at a B_3 "island of stability." The recent development of a novel high-flux boron atom source makes it possible to produce ~ 100 mg quantities of cryogenic solid HEDM containing 5 mole percent boron, primarily atoms.

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